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Volumetric Properties for Ionic Liquid−Sucrose−Water Systems

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ABSTRACT: Densities for 1-allyl-3-methylimidazolium chloride ([Amim]Cl)−sucrose−water solutions were measured at 298.15 K. These data were used to calculate the apparent molar volumes of sucrose ($V_{\Phi,S}$) and [Amim]Cl ($V_{\Phi,IL}$) in the studied solutions. Infinite dilution apparent molar volumes, $V_{\Phi,S}^0$ and $V_{\Phi,IL}^0$, were also obtained, together with the standard transfer volumes of the sucrose ($\Delta_t V_S^0$) from water to aqueous solutions of [Amim]Cl and those of [Amim]Cl ($\Delta_t V_{IL}^0$) from water to aqueous sucrose solution. Additionally, the system studied here was compared with 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4)−sucrose−water mixture. It was shown that the $\Delta_t V_S^0$ and $\Delta_t V_{IL}^0$ values are positive and increase with increasing molalities of ILs and sucrose, respectively, and the $\Delta_t V_S^0$ and $\Delta_t V_{IL}^0$ values have the order of [Amim]Cl > [Bmim]BF_4. Additionally, the volumetric interaction parameters for ionic liquid (IL)−sucrose pairs in water were also obtained and interpreted by the structural interactions model.

INTRODUCTION

Ionic liquids (ILs) are attracting the attention of a growing number of scientists and engineers due to their unique properties. Recently, Wu and co-workers have demonstrated that the addition of sugars to an aqueous solution of a hydrophilic IL produces aqueous two-phase systems (ABS),[1−3] which have great potential use for purification, extraction, and enrichment. These chemical separation processes require reliable and systematic data of thermodynamic properties, such as density. Actually, there exist very few reliable data of liquid densities or excess volumes for IL−sugar−water systems,[4] besides some systematic work done on IL-containing mixtures.[5−12] Additionally, it is very necessary to investigate their volumetric properties to understand the physicochemical process occurring in IL−sugar−water systems, because they can provide information about the structural interactions in solutions.

Herein, the densities of the IL (1-allyl-3-methylimidazolium chloride [Amim]Cl)−sucrose−water systems were measured at 298.15 K, as well as calculation of their apparent molar volumes and volumetric interaction parameters. These results were compared with that of the 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4)−sucrose−water system,[4] and their similarities and differences were explained.

EXPERIMENTAL SECTION

Materials. The sucrose, chlorobutane, allyl chloride, 1-methylimidazole, ethyl acetate, and acetone were all purchased from Shanghai Chemical Reagents Company. They are of analytic grade and used as received. Doubly distilled water was used in all experiments.

Synthesis of [Amim]Cl. [Amim]Cl was prepared based on the reported procedures.[13] Its purity was verified in terms of NMR analysis (> 0.99 mass fraction). The water content of [Amim]Cl (0.2 %) was determined by the Karl Fischer titration (ZSD-2 KF with an uncertainty of 0.05 %, Cany Precision Instruments Co., Ltd.).

Measurement of Density. All aqueous solutions to be studied were freshly prepared by weight with a correction for air buoyancy. The solutions were based on molality with respect to 1 kg of pure water. Relative uncertainties in molality are less than ± 0.03 %. A Westphal balance (PZ-D-5) was corrected with pure water at 298.15 K before measuring the densities of [Amim]Cl−sucrose−water mixtures. The uncertainty in density was estimated to be $\pm\ 2.0 \cdot 10^{-6}\ \mathrm{g \cdot cm^{-3}}$.

RESULTS AND DISCUSSION

Apparent Molar Volume. The density data are given in Table 1. The apparent molar volumes of sucrose, $V_{\Phi,S}$, and IL, $V_{\Phi,IL}$, respectively, were calculated by using the equations:[14]

$$V_{\Phi,\,S} = \frac{M_S}{d} - \frac{(1000 + m_{IL}M_{IL})(d - d_{IL})}{m_S d d_{IL}} \tag{1}$$

$$V_{\Phi,\,IL} = \frac{M_{IL}}{d} - \frac{(1000 + m_S M_S)(d - d_S)}{m_{IL} d d_S} \tag{2}$$

where M_{IL} and M_S are the molar masses of [Amim]Cl and sucrose, respectively. m_{IL} and m_S are the molalities of [Amim]Cl and sucrose, respectively. d, d_S, and d_E are the densities of the [Amim]Cl−sucrose−water, sucrose−water, and [Amim]Cl−water solutions, respectively. Thus, calculated $V_{\Phi,S}$ and $V_{\Phi,IL}$ values are also included in Table 1. Unfortunately, there are no literature values available for comparison.

It has been found that both plots of $V_{\Phi,S}$ against m_S and $V_{\Phi,IL}$ against $m_{IL}^{1/2}$ are completely linear. Therefore, infinite-dilution apparent molar volumes, $V_{\Phi,S}^0$ and $V_{\Phi,IL}^0$, which are equal to the standard partial molar volume values (V_S^0 and V_{IL}^0), are

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Table 1. Densities and Apparent Molar Volumes of Sucrose and [Amim]Cl in Sucrose−Water, [Amim]Cl−Water, and Sucrose−[Amim]Cl−Water Systems at 298.15 K

m_{IL} $\mathrm{mol \cdot kg^{-1}}$	d $\mathrm{cm^3 \cdot mol^{-1}}$	$V_{\Phi,\mathrm{S}}$ $\mathrm{cm^3 \cdot mol^{-1}}$	$V_{\Phi,\mathrm{IL}}$ $\mathrm{cm^3 \cdot mol^{-1}}$	m_{IL} $\mathrm{mol \cdot kg^{-1}}$	d $\mathrm{cm^3 \cdot mol^{-1}}$	$V_{\Phi,\mathrm{S}}$ $\mathrm{cm^3 \cdot mol^{-1}}$	$V_{\Phi,\mathrm{IL}}$ $\mathrm{cm^3 \cdot mol^{-1}}$
$m_{\mathrm{S}} = 0.0200\ \mathrm{mol \cdot kg^{-1}}$				$m_{\mathrm{S}} = 0.1500\ \mathrm{mol \cdot kg^{-1}}$			
0	0.999720	210.978		0	1.016060	212.126	
0.0500	1.000685	211.196	206.319	0.0500	1.016880	211.867	206.382
0.1000	1.001552	211.358	207.218	0.1000	1.017540	212.060	207.365
0.1500	1.002319	211.564	208.060	0.1500	1.018110	212.261	208.229
0.2500	1.003760	211.723	208.939	0.2500	1.019180	212.453	209.119
0.5000	1.007125	212.021	209.580	0.5000	1.021730	212.658	209.709
0.7500	1.010004	212.294	210.094	0.7500	1.023870	212.895	210.207
1.0000	1.012396	212.491	210.618	1.0000	1.025590	213.149	210.746
$m_{\mathrm{S}} = 0.0600\ \mathrm{mol \cdot kg^{-1}}$				$m_{\mathrm{S}} = 0.2000\ \mathrm{mol \cdot kg^{-1}}$			
0	1.004870	211.394		0	1.022120	212.144	
0.0500	1.005780	211.453	206.323	0.0500	1.022850	212.067	206.443
0.1000	1.006580	211.675	207.269	0.1000	1.023430	212.290	207.445
0.1500	1.007280	211.908	208.167	0.1500	1.023920	212.503	208.469
0.2500	1.008600	212.101	209.049	0.2500	1.024860	212.717	209.338
0.5000	1.011710	212.338	209.662	0.5000	1.027120	212.908	209.720
0.7500	1.014360	212.451	210.138	0.7500	1.029000	213.112	210.311
1.0000	1.016530	212.740	210.673	1.0000	1.030480	213.354	210.834
$m_{\mathrm{S}} = 0.1000\ \mathrm{mol \cdot kg^{-1}}$				$m_{\mathrm{S}} = 0.2500\ \mathrm{mol \cdot kg^{-1}}$			
0	1.009900	211.830		0	1.027950	212.599	
0.0500	1.010770	211.645	206.371	0.0500	1.028680	212.274	206.576
0.1000	1.011500	211.910	207.334	0.1000	1.029190	212.484	207.598
0.1500	1.012140	212.116	208.179	0.1500	1.029610	212.695	208.501
0.2500	1.013350	212.322	209.076	0.2500	1.030430	212.878	209.417
0.5000	1.016205	212.524	209.677	0.5000	1.032400	213.107	209.803
0.7500	1.018620	212.777	210.195	0.7500	1.034020	213.334	210.329
1.0000	1.020590	213.044	210.713	1.0000	1.035270	213.563	210.845
[Amim]Cl−Water							
0	0.997100			0.2500	1.001300		141.597
0.0500	0.998100		138.835	0.5000	1.004800		142.501
0.1000	0.999000		139.714	0.7500	1.007800		143.204
0.1500	0.999800		140.605	1.0000	1.010300		143.909

obtained from least-squares weighed fits of the experimental data by the following equations:[15,16]

$$V_{\Phi,\mathrm{S}} = V^0_{\Phi,\mathrm{S}} - S_{\mathrm{S}}{}^{*} m_{\mathrm{S}} \quad (3)$$

$$V_{\Phi,\mathrm{IL}} = V^0_{\Phi,\mathrm{IL}} - S_{\mathrm{IL}}{}^{*} m_{\mathrm{IL}}{}^{1/2} \quad (4)$$

where S_{S}^* and S_{IL}^* are the experimental slopes. The infinite dilution apparent molar volumes for the systems studied are given in Tables 2 and 3. There is no report for $V_{\Phi}{}^0$([Amim]Cl) in any solvent, and therefore our results constitute the first report in this respect.

Volume of Transfer. Standard transfer volumes for [Amim]Cl, $\Delta_t V_{\mathrm{IL}}{}^0$, from water to sucrose−water solutions and those for sucrose, $\Delta_t V_{\mathrm{S}}{}^0$, from water to [Amim]Cl−water solutions were calculated by using values of $V_{\Phi,\mathrm{S}}{}^0$ and $V_{\Phi,\mathrm{IL}}{}^0$, respectively. For comparison, the standard transfer volumes of ([Bmim]BF_4)−sucrose−water mixtures were also calculated from literature.[4] Plots of $\Delta_t V_{\mathrm{S}}{}^0$ and $\Delta_t V_{\mathrm{IL}}{}^0$ against the molalities of ILs and sucrose are represented in Figures 1 and 2, respectively.

As shown in Figures 1 and 2, the values of $\Delta_t V_{\mathrm{S}}{}^0$ and $\Delta_t V_{\mathrm{IL}}{}^0$ for both systems studied are positive and increase with increasing molalities of ILs and sucrose, respectively. This can be interpreted in terms of the structural interaction model proposed by Desnoyers et al.[17] and the group additivity model.[18] According to these models, the interactions between sucrose and ILs can be classified into four types of interactions: (i) cation−R (alkyl groups); (ii) anion−R; (iii) cation−O (O represents OH, C═O, and O groups); and (iv) anion−O interactions. Types i and ii are the hydrophilic−hydrophilic (Hi-Hb) interactions. Type iii is the Hi(+)−Hi(−) interaction, where "+" and "−" indicate respectively electropositive and electronegative. Type iv is the Hi(−)−Hi(−) interaction.

According to the structural interaction model,[17] the interactions of types i, ii, and iv are repulsive because these two groups are incompatible in their structural influence or their tendencies

Table 2. Infinite-Dilution Apparent Molar Volumes ($V_{\Phi,S}{}^0$/cm$^3\cdot$mol^{-1}) of Sucrose in Aqueous IL Solutions and Slopes (SS*/cm$^3\cdot$kg$\cdot$mol^{-2} in parentheses) of eq 3 at 298.15 K

	m_{IL} (mol·kg^{-1})							
IL	0 (± 0.02)	0.0500 (± 0.04)	0.1000 (± 0.02)	0.1500 (± 0.02)	0.2500 (± 0.03)	0.5000 (± 0.03)	0.7500 (± 0.02)	1.0000 (± 0.01)
[Amim]Cl	211.00 (6.42)	211.15 (4.58)	211.37 (4.54)	211.62 (4.36)	211.73 (4.72)	212.06 (4.17)	212.21 (4.51)	212.45 (4.55)
[Bmim]BF_4^4	211.00 (6.42)	211.07 (4.29)	211.26 (4.36)	211.53 (4.04)	211.70 (4.22)	211.92 (4.08)	212.14 (4.16)	212.34 (4.18)

Table 3. Infinite-Dilution Apparent Molar Volumes ($V_{\Phi,IL}{}^0$/cm$^3\cdot$mol^{-1}) of ILs in Aqueous Sucrose Solutions and Slopes (S_{IL}*/cm$^3\cdot$kg$\cdot$mol^{-2} in parentheses) of eq 4 at 298.15 K

	m_S (mol·kg^{-1})						
IL	0 (± 0.01)	0.0200 (± 0.01)	0.0600 (± 0.02)	0.1000 (± 0.04)	0.1500 (± 0.01)	0.2000 (± 0.02)	0.2500 (± 0.03)
[Amim]Cl	137.91 (6.42)	205.74 (4.58)	205.79 (4.54)	205.83 (4.36)	205.86 (5.18)	206.01 (5.12)	206.17 (4.97)
[Bmim]BF_4^4	187.78 (1.67)	187.81 (1.69)	187.91 (1.61)	188.08 (1.45)	188.11 (1.44)	188.21 (1.42)	188.28 (1.37)

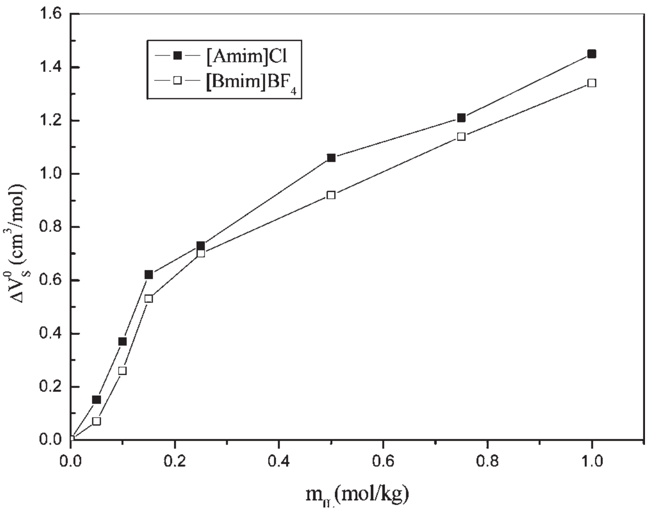

Figure 1. Variation of the standard transfer volumes, $\Delta_t V_S{}^0$, of sucrose from water to aqueous IL solutions with the molality of ILs. ■, [Amim]Cl; □, [Bmim]BF_4.

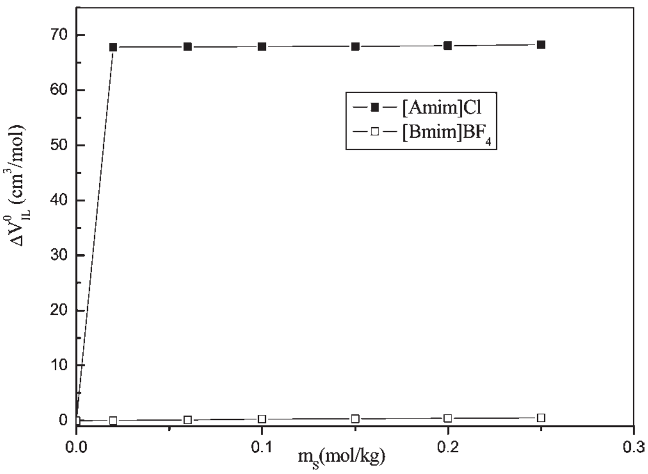

Figure 2. Variation of the standard transfer volumes, $\Delta_t V_{IL}{}^0$, of ILs from water to aqueous sucrose solutions with the molality of sucrose. ■, [Amim]Cl; □, [Bmim]BF_4.

to orient water and consequently contribute a negative volume. Only two groups in type iii are compatible with each other; thus, their interactions contribute a positive volume. Therefore it could be concluded that the interaction of type iii is predominant

On the other hand, Figure 1 shows that values of $\Delta_t V_S{}^0$ at a given m_{IL} have the following order: [Amim]Cl > [Bmim]BF_4. This can be ascribed to the fact the water-structure breaking effects of cations and anions, contributing positively to volumes, are in the order [Amim]$^+$ > [Bmim]$^+$ and Cl$^-$ > $BF_4{}^-$, respectively.

The standard partial molar volume, V_i^0, of sucrose can also be expressed as[19]

$$V_{\Phi,S}^0 = V_{v,w} + V_{void} - V_{shrinkage} \tag{5}$$

where $V_{v,w}$ is the van der Waals volume, V_{void} is the associated void or empty volume, and $V_{shrinkage}$ is the shrinkage in volume caused by interactions of hydrogen bonding groups with water molecules. If $V_{v,w}$ and V_{void} are assumed to have the same magnitudes in water and aqueous IL solutions, positive values of $\Delta_t V_S{}^0$ might arise from $V_{shrinkage}$ in aqueous IL solutions. Since ions of ILs can be hydrated, the presence of ILs in water will decrease the hydration effects of hydroxyl groups of sucrose molecules, thus causing a decrease in $V_{shrinkage}$. This is a reason why $\Delta_t V_S{}^0$ rises with increasing molalities of ILs. The hydration effects decrease in the order of [Amim]$^+$ > [Bmim]$^+$ and Cl$^-$ > $BF_4{}^-$, and therefore values of $\Delta_t V_S{}^0$ should have the order of [Amim]Cl > [Bmim]BF_4 at a given molality of ILs.

Volumetric Interaction Parameters. Volumetric interaction parameters can be obtained by separately fitting experimental data by the following equations:[14,20]

$$\Delta_t V_{\Phi,S} = 2\upsilon\nu_{IS} m_{IL} + 3\upsilon^2 \nu_{IIS} m_{IL}{}^2 + 3\upsilon\nu_{ISS} m_{IL} m_S + \ldots \tag{6}$$

$$\Delta_t V_{\Phi,IL} = 2\upsilon\nu_{IS} m_S + 3\upsilon^2 \nu_{IIS} m_{IL} m_S + 3\upsilon\nu_{ISS} m_S{}^2 + \ldots \tag{7}$$

where $\Delta_t V_{\Phi,S}$ and $\Delta_t V_{\Phi,IL}$ are, respectively, the transfer volumes of sucrose at molality m_S from water to a solution of electrolyte at molality m_{IL} and of ILs at molality m_{IL} from water to a solution of saccharides at m_S. Here, υ is the number of ions into which the electrolyte dissociates, and ν_{IS}, ν_{IIS}, and ν_{ISS} are pair and triplet interaction parameters. The interaction parameters were

Table 4. Volumetric Interaction Parameters for IL−Sucrose−Water Systems at 298.15 K

	$2v\nu_{IS}$	$3v\nu_{ISS}$	$3v^2\nu_{IIS}$	σ^d
IL	$cm^3 \cdot mol^{-2} \cdot kg$	$cm^3 \cdot mol^{-3} \cdot kg^2$	$cm^3 \cdot mol^{-3} \cdot kg^2$	$cm^3 \cdot mol^{-1}$
[Amim]Cl	2.760 ± 0.025	−0.327 ± 0.018	−3.183 ± 0.050	0.04
[Bmim]BF$_4$[4]	2.208 ± 0.032	−1.882 ± 0.015	−0.971 ± 0.035	0.03

obtained by least-squares regression from these two equations, respectively. Since the values from the two equations are in good agreement with each other within experimental error, their mean values are taken as the final values and are given in Table 4 together with their standard deviations.

The results show that both ν_{IS} values are positive. This can be interpreted on the basis of the structural interactions model proposed Desnoyers et al.[17] and the hydration model by Conway.[21] The positive ν_{IS} values are mainly due to the cation−O interaction, since the dehydration of $[Amim]^+$ or/and $[Bmim]^+$and O contribute a positive value to the volume. On the other hand, we noted that the ν_{IS} value for the [Amim]Cl−sucrose pair is larger than that for [Bmim]BF$_4$−sucrose, as expected.

CONCLUSIONS

In this work, we investigated the volumetric properties of [Amim]Cl−sucrose−water mixtures and made a comparison with a system of [Bmim]BF$_4$−sucrose−water. It was shown that values of $\Delta_t V_S{}^0$ and $\Delta_t V_{IL}{}^0$ are positive and increase with increasing molalities of ILs and sucrose, respectively. Overall, the $\Delta_t V_S{}^0$ and $\Delta_t V_{IL}{}^0$ values have the order of [Amim]Cl > [Bmim]BF$_4$. In addition, we found that the volumetric interaction parameters ν_{IS} is positive for both studied systems, and as expected, the value of ν_{IS} for the [Amim]Cl−sucrose pair is larger than that for [Bmim]BF$_4$−sucrose. It could be concluded that the interaction of cation−O is predominant.

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